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Original Research Article

Assessment of Selected Physico-Chemical Properties and Metals in Qeera Stream Water, Bakkee-Jamaa, Nekemte, Ethiopia

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ABSTRACT

In this paper, *Qeera* wastewater containing stream, found in *Bakkee-Jamaa* district of *Nekemte* town, was assessed for selected metals and physico-chemical properties. The metals were determined by flame atomic absorption spectrophotometry (FAAS). Additional water samples collected from *Dangi* spring water, which is found about 10 km far away from the town, and *Chalalaqi* waste water containing stream were also assessed for reference. Analysis of concentration of Pb, Cd, Cr, Ca, and Ni metals were carried out using FAAS. For metal analysis good linearity were obtained with coefficient of determination (R^2) 0.998 or better. The LOD for the metals were in the range of 0.003 to 0.018 mg L⁻¹ and LOQ, 0.010 to 0.06 mg L⁻¹. Recovery studies ranged from 92 % to 104 % for the metals. The study shows that Ca, Cd and Ni are quantified in all the three water bodies. Overall, the level of the metals studied is higher in the urban area streams than that of *Dangi* spring in the rural area. The average concentrations (in mg/L) of Ca, Cd and Ni were found to be 9.56., 0.22 and 0.38, respectively. When compared with international guide lines for the quality of irrigation water, Cd and Ni are above permissible levels and show significant pollution of the water. The data obtained from the study of selected physico-chemical properties (EC, TDS, pH, TSS and Cl⁻) of the water samples were found to be within the recommended level except TSS.

Keywords: Selected Metals, Physico-chemical properties, *Qeera* stream water, Contaminants.

Introduction

Surface water available in ponds, streams, rivers, lakes and dams is used for drinking, irrigation, power production, etc. Rivers constitute major surface water sources for domestic, agricultural and industrial purposes and are essential for the development of human civilization. Surface waters are most exposible to pollution due to their accessibility for disposal of wastewaters [1]. Major urban inputs to sewage water include household effluents, drainage water, business effluents, atmospheric deposition, and traffic related emissions transported with storm water into the sewerage system [2-4]. Urban wastewater pollution sources are very variables, depending on the levels of development, population and the location of the urban area. Most communities generate wastewater from both residential and non-residential sources. Other categories of wastewater sources are generated with four sources (1) municipal wastewater; (2) industrial wastewaters, (3) agricultural wastewater and (4) storm-water runoff. The municipal wastewater consists of a combination of domestic wastewater, originating in households, offices, and public restrooms, and lesser contributions from many commercial and small industrial sources [5-9]. Municipal wastewater potentially contains nutrients for agriculture [10,11]. Farmers still prefer using sewage for irrigation, by reason of its nutritive value, which reduces expenditure on chemical fertilizer. However, potential toxic substances are usually found in wastewater, which may limit the long-term use of wastewater for agricultural purpose [12,13]. Unless properly treated, wastewater can harm public health and the environment. Of the pollutants, heavy metals can endanger public health by being incorporated into food chain [14]. Heavy metals are not biodegradable and tend to accumulate in the sediments of waterways in association with organic and inorganic matter [15]. Food chain contamination by toxic metals has become a burning issue in recent years because of their potential accumulation in bio-systems through contaminated water, soil and air [16]. As it has been examined by a number of researchers, wastewater contains major toxic metals, such as Hg, Cd, Pb, as well as potentially toxic metals including Cu, Zn, Fe, Ni, and Cr(VI) [17]. The accumulation of heavy metals such as Cr, Fe, Mn, Cu, Zn, Ni and Pb in plants is significantly increased by sewage water irrigation [18, 19]. Continuous irrigation with wastewater could lead to accumulation of salts, plant nutrients and heavy metals in soils beyond crop tolerance levels. Thus, there is need for sustained studies in order to fully

analyze and understand the long term environmental impacts of the use of sewage water for crop irrigation [20].

Nekemte is a central town of East Wollega administrative zone. There are several streams which are contaminated by sewage water, dry and wet disposals in the town. Peoples living in the area use the stream water for irrigation especially during dry seasons (winter), for cultivation of maize, and vegetables such as cabbage, potato, carrot, and so on. These vegetables and maize are widely consumed by peoples in the town. In addition to these, domestic animals in some of the villages use such stream water for drinking. Streams used for irrigation in Nekemte town are found in many sites including *Qeera* and *Chalalaqi*. *Qeera* stream emerges from several small springs that flow out of the central part of the town and moves in the lower plain between the hillsides to the west of the town parallel to the main road to *Gimbi*. There is large quantity of domestic sewage discharged to the stream from hillside residents. The main objective of this study was to evaluate the level of selected metals and assess some physicochemical properties of *Qeera* stream in Nekemte town.

Materials and methods

Study area and sample collection.

Qeera site is the district in Nekemte town in which the slaughter house of the town is found. The stream water which comes from the center of the town flows on the back side of the slaughter house. So, the name Qeera comes after the house. The study area is indicated in Fig.1. The waste water samples were collected only in one season at the beginning of February in 2017. The sample collection was carried out from different locations downstream from east to west direction (at the source of the spring, at middle site within densely populated stream sides, downstream at the out let from the town). One of the source springs is labeled as location 1, the middle site is labeled as location 2 and the town out let site is labeled as location 3. These three sites are indicated on the figure as Location A: 9°05'11.10" N, 36°32'42.96" E, 2088.8 m; Location B: 9°05'08.06" N, 36°32'15.07" E, 2081.2 m; Location C: 9°05'01.54" N, 36°31'52.62" E, and 2064.1 m. Difference in composition of the water during the day time was attempted to be considered by collecting the water samples once in the morning and once in the afternoon. The water samples were collected along the water way in plastic bottles and 1% of

concentrated HNO_3 was added to the samples to avoid microbial activity. Water samples from *Dangi* spring which is located 10 km from Nekemte town and waste water samples from *Chalalaqi* irrigation site were also collected in the same manner. These additional samples are used for comparison of results. The pH, time, date and place of collection were indicated on the sample containers. The samples were transported to laboratory and stored in refrigerator at 4°C . To assess the physico-chemical properties of *Qeera* wastewater containing stream, composite sample were taken in 2 L prewashed plastic bottle.

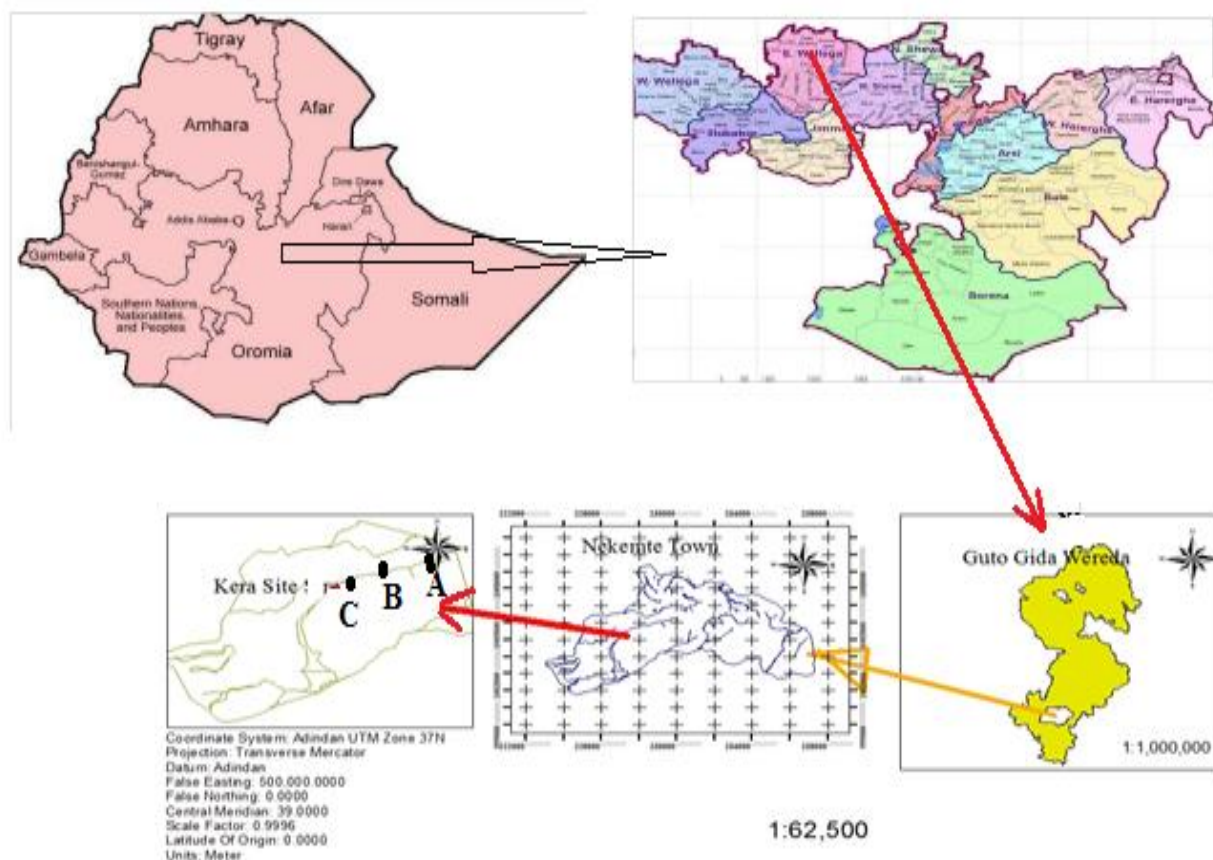


Figure 1. Location map of Nekemte *Qeera* stream (Sample collection sites, Location A: $9^{\circ}05'11.10''$ N, $36^{\circ}32'42.96''$ E, 2088.8 m; Location B: $9^{\circ}05'08.06''$ N, $36^{\circ}32'15.07''$ E, 2081.2 m; Location C: $9^{\circ}05'01.54''$ N, $36^{\circ}31'52.62''$ E, 2064.1m)

Instrumentation and Apparatus. Flame atomic absorption spectrophotometer (AAS) (model- ZEE nit 700 p, analyticjena made in Germany), equipped with deuterium arc background correctors and air/acetylene fuel was used for the analysis. Other equipments used in the experimentation include hot plate, pH-meter (pH-009 (I)), micro processor based conductivity meter (EC/TDS meter, model-1601).

Chemicals, Reagents and Standard Solutions. Chemicals and reagents that were used in the analysis are all analytical grades. 70 % HNO_3 , (SpectroSol, BDH, England) and 70 % HClO_4 (Analar ®, BDH, England) were used for digestion of the water samples. Lanthanum nitrate hydrate (99.9 %, Aldrich, Muwaukee, USA) was used for releasing calcium from the sample. Stock standard solutions of the metals (Ca, Cr, Ni, Pb, and Cd) (1000 mg L^{-1} , PURO-GRAPHIC[™] calibration standards, BUCK SCIENTIFIC prepared as nitrates for each element in 2% HNO_3) were used for the preparation of calibration curves for the determination of metals in the samples. De-ionized water was used for cleaning of glassware and dilution of sample solutions. Intermediate standard solutions were prepared from the standard stock solutions. These intermediate standards were diluted with distilled water to obtain working standards for each metal of interest.

Assessment of selected physico-chemical properties

The pH was measured in situ at the sampling site. The composite sample from each location was immediately transported to Wollega University laboratory after sampling and four of the physicochemical parameters (EC, TDS, TSS, Cl^-) were determined immediately. For calibration of EC/ TDS instrument, standard reference solution of 0.01M of KCl was prepared by dissolving 0.745 g of KCl, which had the specific conductance of $1.413 \mu\text{S/cm}$. The calibrated EC/TDS –meter electrodes were rinsed by de-ionized water and inserted in the water sample at $25 \text{ }^\circ\text{C}$. The conductance was taken by direct reading in μS ; the instrument is adjusted to display TDS of the sample in ppm. In the Argometric method, standard solution of potassium chromate indicator was prepared by titrating with 0.0141N AgNO_3 . To determine the Cl^- concentration, 4 drops of potassium chromate indicator was added to 50 mL of water sample and titrated by known volume of 0.0141 M AgNO_3 . Blank sample were also titrated in the same procedure with the sample.

To determine the mass of TSS in wastewater sample, first the mass of filter paper was weighed and recorded as B. The filter paper was inserted into a disk with wrinkled side up in filtration apparatus. 100 mL of water sample was taken and poured into filtration apparatus. The residue with the filter paper was placed in evaporating dish and put in oven for 1hr; this was removed and placed in desiccators for 20 min. The dried one was weighed and the result was recorded in grams, marked as A.

$$TSS \text{ in } mg/L = \frac{(A - B)}{\text{Volume of sample taken}} \times 1000$$

Sample digestion.

100 mL aliquot of well-mixed sample was transferred into a beaker. 2 mL of concentrated HNO₃ and 5 mL of concentrated HCl were added and heated at about 95 °C until the volume has been reduced to 15-20 mL[21].

Sample analysis by FAAS.

The acid digestions as well as the analysis of the water samples were conducted at the Research Laboratory of Addis Ababa University. The clear solutions of digested water samples were analyzed using FAAS for the concentration of metal of interest. The instrument was calibrated using series of working standards. For the determination of metals in the water samples, four series of standard metal solutions were prepared by diluting the stock solutions of the metal with de-ionized water. Six replicate determinations were carried out on each sample.

Result and discussion

3.1 Analytical performance characteristics of FAAS . The basic parameters that characterize the performance of an analysis, namely, linearity, LOD, LOQ, recovery, and precision are presented in Table1.

Table 1. Analytical performance of FAAS in the analysis of selected metals

Metal	Linearity (R²)	SD* of blank (n=7)	MDL (mg L⁻¹)	LOQ (mg L⁻¹)	Recovery (%)	Instrument Detection Limit (IDL)
Ca	0.999	0.003	0.009	0.030	104 ± 0.28	0.005
Cd	0.999	0.002	0.006	0.020	99 ± 1.22	0.002
Cr	0.999	0.004	0.012	0.040	97.3 ± 3.23	0.005
Ni	0.998	0.006	0.018	0.060	98 ± 0.06	0.014
Pb	0.999	0.001	0.003	0.010	92.6 ± 6.18	0.003

*SD = Standard deviation

3.2 Metal analysis of the water samples. The data obtained from the metal analysis is summarized in Table 2. The samples collected from different locations of Qeera downstream were analyzed separately. Among the five metals analyzed, three of them (Ca, Cd and Ni) were detected and two of them (Cr and Pb) were not detected in the water samples collected from all the sites. The concentration levels of the detected metals are different in the sampling locations along Qeera stream.

The data shows that there is increment in concentration of Ca from location 1 to location 2. This could be due to the low level of Ca in ground (spring) water. The increment at location 2 could be due to addition of waste water from house disposals, sewages and discharges from the surroundings. At some extent, the observed reduction in the concentration of Ca down the stream at lower location seems due to dilution, and bounding of Ca with other organic and inorganic ions in the stream and sediment at the bottom.

Table 2. Average concentrations of metals determined by FAAS (in ppm)

Metal	Qeera stream				References	
	Location 1	Location 2	Location 3	Average	Chalalaqi	Dangi
Ca	4.09±0.036	14.14±0.060	10.45±0.098	9.56	5.65±0.021	1.16±0.003
Cd	0.20±0.000	0.23±0.000	0.23±0.000	0.22	0.23±0.000	0.22±0.001
Cr	ND*	ND	ND	-	ND	ND
Ni	0.23±0.001	0.50±0.004	0.42±0.013	0.38	0.47±0.001	0.31±0.000
Pb	ND	ND	ND	-	ND	ND

*ND = Not detected

Ni was the second trace metal analyzed and quantified in this research. This study indicates different location of Qeera stream contained different concentration of the metal. Ni concentration was low at the source spring; it became higher at the middle and decreased at the end. As mentioned above, dilution can be the reason for the decrease at the lower location.

Different concentration of Cd metal is also quantified in stream water samples from different locations of Qeera stream. The trend of change of concentration level of Cd is similar to that of Ca and Ni. The observation that need to be noted is that the levels of Cd and Ni content in location 2 is increased probably due to the accumulation of Cd and Ni metals in ground water as a result of disposals of Cd-Ni batteries. As assessed by Fisseha et al. (2016) [22] domestic wastes like detergents and particulates materials are responsible for polluting urban runoff and consequently increase the concentrations of heavy metals in the river at the mid-stream. As compared to that of Ca the average levels of Cd and Ni is low in three stream sites. This indicates that Ca containing wastes are abundant that needs further study. Cr and Pb metals were generally not detected; this is reasonable since there is no industry that could be a potential source of the metals. Generally, the three locations (Qeera, Chalalaqi and Dangi) have similar concentration level of Cd and Ni (Fig 2.). Literature reports show significant positive relationships between Cd and Ni [23]. However, they differ in their calcium concentration. It can be noticed that Dangi spring has low concentration of the detected metals. This could be true since Dangi is found in rural area and is less exposed to waste disposal that possibly change the natural mineral composition of the region. A potential environmental source of the Cd is through diffuse pollution caused by contamination through the use of agricultural phosphate fertilizers which may contain up to 100 mg L⁻¹ Cd due to the presence of Cd in the phosphate rock used for their

manufacture [24]. So, the Cd concentration quantified in Dangi spring is possibly from use of fertilizers in farm land in the rural area.

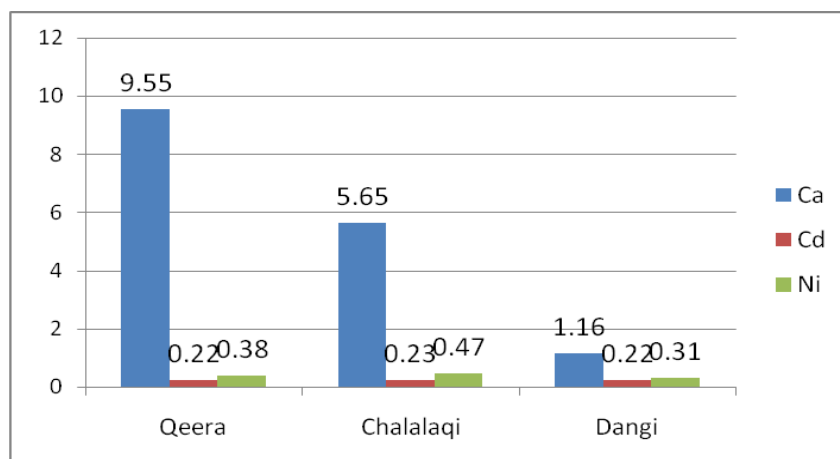


Figure 2. Graphical presentation of the trends in concentrations of the detected metal in Qeera, Chalalaqi and Dangi water samples

The average values of the metals analyzed compared with maximum permissible limits for irrigation waters [25] are indicated in Table 3. It is observed that that the water studied is safe with respect to the Ca analyzed. However, Cd and Ni are above permissible levels and show significant pollution of the water. In plants, heavy metals such as cadmium, lead and nickel are greatly toxic at comparatively low amount. Greater quantity of heavy metals in soils has been testified to prevent plant's progress in growth; uptake of nutrients, physiological as well as metabolic processes. Plants and animals take up metals from contaminated soil and water as well as from deposits on parts of the plants exposed to the air from polluted environment [26].

Table 3. Comparison of the concentration of the metals studied with international guideline

Metals	Qeera	Chalalaqi	Dangi	MPL* (EPA, 2012) (mg/L)
Ca	8.8	5.65	1.16	-
Cd	0.22	0.23	0.22	0.01
Ni	0.38	0.47	0.31	0.2

Selected physico-chemical properties of the water samples.

Data of physico-chemical parameters obtained in the current study is displayed in Table 4. According to the finding, the studied water is safe for irrigation with respect to the parameters considered here.

Table 4. Selected physico-chemical properties of Qeera stream

	pH	EC (mS/cm)	TDS (mg/L)	TSS (mg/L)	Cl⁻ (mg/L)
Study area	6.8±0.36	0.233±0.01	148.95±1.62	325.7±0.56	19
MPL*	6.5-8.4	< 0.70	< 450	< 100	< 142

MPL* = Maximum permissible level [27]

Conclusion and recommendation

The present study analyzed the level of calcium, lead, cadmium, chromium, and nickel in Qeera stream water and compared with that of Chalalaqi stream and Dangi spring waters. Only calcium, cadmium, and nickel were quantified. The result showed that, the metal concentration of the metals at three different locations of Qeera stream varied by a trend that shows an increase up to the middle part and then a decrease at the lower site at the out let from the town. The study indicates that the waste disposal in urban area causes some change in the level of the studied metals in the physical environment. Among the three quantified metals Ca was found to be less than maximum permissible limit recommended by FAO. But Cd and Ni were found to be above the recommended tolerance level. The physico-chemical parameters selected for the current study (EC, TDS, pH, and Cl⁻) were found to be within the recommended normal quantity except TSS. These indicate the waste discharged to the Qeera stream contaminated by causing severe TSS and toxic metals such as Cd and Ni.

It is recommended that additional study is required on the other physico-chemical properties including biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), phosphate and nitrate as well as certain metals such as Na and K. Future studies should also consider seasonal variation.

Urban streams should be protected from contamination by toxic metals that are generated from waste disposals and sewages from various point and spatial sources of pollutants. To this end, the

administrative offices as well as the residents of the locality have to take responsibility to change the futurity of streams in the town. To change the people's custom of waste disposal, awareness creating mechanisms has to be applied by all concerned bodies.

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Conflict of Interest The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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